

**Determination of the Interfacial Surface Energy of Succinonitrile
Using Surface Light Scattering Spectrometer¹**

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ABSTRACT

Liquid/vapor interfacial surface energies of succinonitrile, $\text{NC}(\text{CH}_2)_2\text{CN}$, were measured using non-invasive Surface Light Scattering (SLS) spectroscopy. Succinonitrile (SCN) has been and is being used extensively in materials science and fluid physics research, for example, in several theoretical and numerical studies of dendritic growth. It is an established model material with several essential physical properties accurately known with the exception of the liquid/vapor surface tension, γ_{lv} at various temperatures. Using the Surface Light Scattering Spectrometer, we have experimentally determined the liquid/vapor surface tension of SCN in the temperature range from just above its melting point (58.1°C) to 110°C using this non-invasive method. Previous measurements of SCN surface tension are extremely limited. To the best of our knowledge, this work is the first to measure the interfacial energy of succinonitrile non-invasively at melt and elevated temperatures. The SLS spectroscopy is relatively new and unique. This technique has several advantages over classical methods: it is non-invasive, has good accuracy, and measures the surface tension and viscosity simultaneously though the viscosity results are not presented here. The accuracy of values obtained from this technique on some standard liquids is better than 2% for interfacial energy and about 10% for viscosity. Our measurements gave $\gamma_{\text{lv}} = 42.28 - 0.0629T$ (mN/m), with T in units of Celsius for pure SCN.

KEY WORDS: Interfacial Energy, Succinonitrile, Surface Light Scattering Spectroscopy, Surface Tension

1. INTRODUCTION

Succinonitrile, a widely used metal analog, has been an established sample material with several key physical properties accurately known.^{1, 2,3} Several characteristics make succinonitrile advantageous for use as a model material: it is optically transparent, has a BCC crystal structure, has a low melting point, and has only slightly anisotropic solid/liquid interfacial energy, γ_{sl} , thus it solidifies dendritically. In the analysis of phase transformation and flow, including nucleation, dendritic growth, interface stability, Ostwald ripening, and Marangoni flow, SCN has been used extensively as a model material. The interfacial energy an important physical parameter in many of these analyses. Surface tension driven convection (Marangoni convection) is a subject of significant interest from both fundamental and technological points of view. Reliable liquid/vapor surface tension, γ_{lv} , data at various temperatures for SCN and SCN-acetone alloys is needed, for example, for studying the effect of Marangoni convection generated by voids on segregation during the solidification process.⁴ The change in γ_{lv} with temperature is the driving force for Marangoni flow, thus reliable interfacial energy values at melt and above the melting point are essential.

*Lange's Handbook of Chemistry*⁵ provides a linear temperature relationship for pure SCN citing data obtained from the capillary rise method which is cited in Jasper.⁶ One other data set was found in the literature from Walden.⁷ These data sets were quite different. Experimental γ_{lv} values of SCN-acetone alloys could not be found in the literature. Our measurements are the first known non-invasive measurements for SCN at different temperatures. We have demonstrated in this present work that interfacial energy measurements of succinonitrile at different temperatures can be measured relatively easily using this non-invasive Surface Light Scattering Spectroscopic technique.

2. INTERFACIAL ENERGY AND VISCOSITY MEASUREMENTS USING SURFACE LIGHT SCATTERING SPECTROSCOPY

2.1. Standard Surface Tension Measurement Techniques

Techniques commonly used to measure the surface tension of liquid/vapor interfaces can be classified as either equilibrium or dynamic measurements.⁸ One of the most common equilibrium techniques is the ring method, or the du Noüy method. This measurement uses a ring of platinum or platinum-iridium wire to stretch a portion of the liquid surface. The force needed to accomplish this is measured. Another similar method to the above method, but still an invasive technique, is the plate method, or better known as the Wilhelmy method, which makes use of a platinum rectangular plate. Other equilibrium methods include capillary rise and pendant drop. Techniques for performing dynamic γ_{lv} measurements include the maximum bubble pressure, oscillating jet, and drop volume methods.

These techniques suffer from the need to disturb the liquid or liquid surface, introducing a mechanical disturbance, which can lead to erroneous results. They all require very precise measurements of parameters that are not easily measured. Several also require a correction factor that is difficult to measure. All in all, an easier-to-use and more accurate test method is desirable. Surface Light Scattering (SLS) measurements of several standard liquids, such as water, ethanol and acetone, have shown the SLS techniques developed to be accurate to better than 2% for γ_{lv} and 10% for viscosity.^{9,10} Another advantage of SLS spectroscopy is that it does not introduce any mechanical or thermal disturbance to the liquid or the liquid surface. It also allows for dynamic measurements unlike many surface tension measurement techniques which have a long response time.

2.2 Determination of Surface Tension and Viscosity Using Surface Light

Scattering Spectroscopy

Determination of surface tension and viscosity can be made from the non-invasive measurement of the coherent light scattered from capillary waves generated by thermally excited surface ripples. The theoretical estimate of the amplitude of these surface ripples is on the order of a tenth of an Angstrom to a few nanometers. The study and observation of the scattered light from the ripples was first introduced by Ketyl and Ingaard^{11,12} and a brief history is given in Langevin's book.¹³ This method measures the power spectrum of a narrowly selected group of the surface waves with wavelengths on the order of a tenth of a millimeter, corresponding to frequencies between about 1 kHz and 50 kHz, depending upon the material and temperature. The surface tension and viscosity are then deduced from the acquired autocorrelation function.

In short, the power spectrum, $P(\omega)$, of the ripples for a given k -vector is contained in the photodetector current measurement and is approximately given by the Lorentzian relation

$$P(\omega) = a_0 \left[\frac{\Gamma}{\Gamma^2 + (\omega - \omega_0)^2} + \frac{\Gamma}{\Gamma^2 + (\omega + \omega_0)^2} \right] \quad (1)$$

where ω_0 is the center frequency, Γ is the full width at half height, and a_0 is a scaling constant.

The center frequency, ω_0 , and full width at half height, Γ , are related to the surface tension and kinematic viscosity through the dispersion relation. In the first-order approximation to the solution of the Navier-Stokes equation, these relationships are given by

$$\omega_0(k) = \left(\frac{\gamma}{\rho}\right)^{1/2} |k|^{3/2} \quad \text{and} \quad \Gamma = 2|k|^2 \nu \quad (2)$$

where ρ is the density of the liquid, ν is the kinematic viscosity ($\nu = \nu_d/\rho$ where ν_d is the dynamic viscosity), and k is the wave vector where $k = 2\pi/a$ and a is the grating constant.

The power spectrum in equation (1), is related to the autocorrelation function $R(\tau)$ in the time domain by the Weiner-Khintchine theorem and has the form:

$$R(\tau) = A + B \cos(\omega_0 \tau) \exp(-\Gamma \tau) \quad (3)$$

where A and B are constants and τ is time. Equations (1) and (3) represent measurements which are free from instrumental broadening. Instrumental broadening is common in these types of measurements and is caused by 1) the fact that the laser transverse mode is not completely Gaussian, and 2) the Fourier optics are not exactly aligned. The result is that more than a single scattered light beam (several k -vectors) combines with the reference beam from the diffraction grating. In most cases, the effect of instrumental broadening is so small that it can be described as a convolution of the Lorentzian spectrum with a Gaussian spectrum assuming that the intensity profile of the laser is generally Gaussian in shape. Equation (3) then becomes:

$$R(\tau) = A + B \cos(\omega_0 \tau) \exp\{-\Gamma \tau - (\beta \tau)^2/4\} \quad (4)$$

when instrumental broadening is taken into account where β is the half width at half height of the Gaussian spectrum.

The laser heterodyne method (also known as light beating spectroscopy) is used in SLS by introducing a local oscillator to beat against the scattered signal. As interest grew in the characterization of thin films and monolayers, the observation of critical point phenomena, and the study of biological membranes, this non-invasive laser heterodyne technique progressively

improved. Hård, *et al.* developed a surface light scattering system consisting of a grating placed in the optical beam path to create a constant local oscillator.⁹ The idea behind this was to project the image of the grating on a liquid vapor interface and heterodyne beat the scattered signal with the higher order diffracted beam at the detector plane. This approach provides a constant value local oscillator for heterodyning. It also selects the scattered k-vector, which is an essential factor in the dispersion relation equation when deducing the surface tension and viscosity. References 13 and 14 give the detailed theory of surface fluctuation spectroscopy using the grating heterodyne detection method. The analysis of the grating heterodyne system by Edwards, *et al.*¹⁴ and Lading *et al.*¹⁵ provided the corrections required in the data analysis algorithm. Hardware for earlier versions of this heterodyne system was very large and heavy. We have designed, built, and tested a compact, lightweight, and better performing system using a semiconductor laser and associated opto-electronics for this work.

An alternative way to detect the light scattering from thermal ripplon waves is to split a low intensity beam from the main incident laser beam and combine it with the scattered signal before it is mixed at the photodetector. Since both the local oscillator light and scattered light originated from a common laser source whose output is split and recombined down-stream, a delay line is inserted into one of the beam paths to compensate for any path differences, thus allowing perfect phase matching, mandatory for optical heterodyning. Mazur *et al.* used this type of spectrometer to measure surface properties of liquid/vapor interfaces.¹⁶

Figures (1) and (2) show the schematic diagrams of SLS spectrometers for transmission and reflection type measurements, respectively. Functionality of both designs are the same except Fig. (1) is better for transparent materials since forward scattering has higher intensity and the system is theoretically seven times less vibration-sensitive than the reflective system.^{17,18}

Basically, a coherent light source such as a laser illuminates a phase grating, diffracting about 1% of the light power into the first-order beams. The grating is then imaged onto the liquid vapor interface with a pair of Fourier transform lens. Part of the first-order beam from the grating (only one is needed) directly transmits through the surface as the reference beam. The angle between these beams and the liquid surface selects the wave vector k of the ripplon wave to be studied. Lenses in the output plane serve as Fraunhofer imaging at the back focal plane and also as a tele-lens for angular separation of the first and the zeroth-order beams. The first-order beam is directed onto the photodetector and the photocurrent is amplified, filtered and finally processed in an autocorrelator or a spectrum analyzer.

3. EXPERIMENTAL SETUP AND MEASUREMENTS

Since SCN is an optically transparent material, we used the transmission type spectrometer shown in Figure (1). The SCN was transferred to an optically clear sample container, and the temperature controllers and heaters were added during the experimental setup. A heater at the bottom of the sample container was used to heat the SCN, and a heater at the top of the container was used to prevent SCN condensation on the top surface, which would interfere with the beam. To obtain the sample temperature correctly a small thermocouple was inserted in the sample. The laser light source used was a gain-guided, broadband, semiconductor laser diode at a wavelength of 670 nm. For surface light scattering, the theoretical calculation of the required coherence length is about 70 μm provided that the surface ripplon amplitude ranges from 0.1 Angstroms to 10 nm.⁹ The diode was powered by the LDC-3742B ILX Lightwave Laser Diode Controller. A thermoelectric cooler was set to maintain the laser diode at a constant temperature for power stability during operation. The beam then illuminated a diffraction grating with a

grating constant of 250 cm^{-1} developed by Risø National Laboratory. This grating could be adjusted to diffract between 0.5% to 10% of the light into the first-order beams. This made it easier to isolate and strengthen the intensity of a first-order beam at the photodetector downstream.

A single first-order beam from the grating, heterodyned with a scattered light beam, was directed into the Analog Modules, Inc., photodetector, model 341-4-INV. Signal amplification and filtering was accomplished by using an EG&G Princeton Applied Research Model 5113 Pre-Amp filter. The correlator card we used was by Brookhaven Instruments Corporation, model BI 9000. The entire apparatus was mounted on the vibration isolated optics table.

Figure (3) shows the time correlation function and Figure (4) shows the power spectrum of the SCN liquid/vapor interface measured at 70°C by this technique. The correlation functions were obtained from the Brookhaven Instruments BI 9000 autocorrelator card at different temperatures. The correlation functions were then loaded into an APL 2000 software program that performs a nonlinear least squares fit on the correlation function, equation (4), and calculates the residual. The center frequency, ω_0 , was determined from this fit. The software can also perform the Fourier transform of the correlation function to obtain the power spectrum, which has the shape of a Lorentzian per equation (1). The center frequency ω_0 , can also be determined in this manner. In both cases, the surface tension is calculated using a more complex version of equation (2). A more detailed explanation of this rigorous approach can be found in Langevin¹³ and Edwards *et al.*¹⁴ The full dispersion equations are obtained by solving the linearized Navier-Stokes equation of continuum hydrodynamics with proper boundary conditions accounting for normal and tangential stress at the interface and a mass balance at the surface. This derivation also accounts for an additional correction term for the instrumental broadening effects.

Calibration experiments were also performed with the apparatus prior to the measurement of SCN at different temperatures. The surface tension of water, acetone, and toluene were measured and compared to the National Bureau of Standards values and they agreed to better than 2% for the surface tension and about 10% for viscosity.^{9,10}

Since the surface light scattering method measures thermally driven ripplons, an estimate of the temperature rise in the SCN due to absorption of the laser beam was considered. The rate of temperature increase, ΔT can be expressed as

$$\Delta T = \alpha(\text{laser power/volume})(\text{MW}/C_p \rho). \quad (5)$$

For this apparatus, a 100 mW laser beam with a cross section of 7 x 2.5 mm was imaged on the surface of the liquid. The liquid depth was 5 mm. The molecular weight (MW) of SCN is 80.09 g/mole. The heat capacity (C_p) is 160.18 J/mol K, and the density (ρ) is 0.988 g/cm³ at the melting point. The absorption (α) of SCN was measured experimentally. The power of the laser beam exiting the sample container with the SCN was compared to the power of the laser beam exiting an empty sample container. The result was an absorption of 2.985% of the laser incident beam by the SCN. Therefore, the calculation of ΔT in equation (5) yields 0.017 K/s for the volume of SCN in the path of the laser beam (0.0875 cm³). Since measurements could be taken in 15 seconds, the temperature change is negligible.

4. RESULTS AND DISCUSSION

There were limited data in the literature on the surface tension of SCN at various temperatures. A relationship was found in the *Lange's Handbook of Chemistry*⁵ as $\gamma = a - bT$ where a and b are constants from a least squares fit and T is the temperature in degrees Celsius. For SCN, $a = 53.26$ and $b = 0.1079$. The data for this linear fit were cited in

Jasper⁶ and the technique mentioned was the capillary rise method. The Jasper article incorrectly references Timmerman and Hennaut-Roland¹⁹ as the source of the data, but it is actually a different Timmerman and Hennaut-Roland reference.²⁰ This source further referenced the data to an untraceable source. The Lange⁵ article also contained one data point at 80°C and referenced to five articles in *Z. Ph. Ch.* published between 1906-1911 by Walden. One of these articles contained data for surface tension of SCN at two other temperatures as well.⁷

Figure (3) also shows the residual curve of the nonlinear least squares fit to the time correlation function as calculated by the APL software. It is from this fit that the center frequency, ω_0 , was calculated, and from which the surface tension was determined using equation (2) with corrections from Edwards *et al.*¹⁴ The SCN density data used in the calculations was obtained from Beilsteins Handbook of Organic Chemistry.²¹ The least squares fit to this data yielded the density relationship, $\rho = -0.00075T + 1.0317$ where T is temperature in degrees Celsius. As stated earlier, the Lorentzian line shape of the power spectrum in Figure (4) can also be used to calculate the center frequency and surface tension. As a note, values obtained for the center frequency were on the order of 1 kHz and those for the full width at half height were a few hundred Hz.

Over a two-month period, a total of 8 data sets were taken and evaluated to determine the surface tension of SCN at various temperatures. Two of these data sets had large residuals and were subsequently discarded. Linear regression fitting and rigorous statistical analysis has been performed after pooling the six data sets and the resulting fit equation was obtained, for T in degrees Celsius,

$$\text{Surface Tension (mN/m)} = 42.28 - 0.0629T. \quad (6)$$

Table 1 lists the surface tension as predicted by equation (6) as well as the calculated data from the equation in Lange⁵ and the three data points from Walden⁷ for comparison. This data is plotted in Figure (5). The relationship established in equation (6) by these experiments yield surface tension data that is about 17% below the Lange relationship⁵ and about 9% above the Walden data.⁷ Statistics were performed on the regression curve fit of equation (6) to bound the confidence level on the fit itself and to confirm a temperature dependence for the surface tension. The result was that there is a 99.95% confidence level that the slope of the regression line is not zero, indicating that the data shows that the surface tension is a function of temperature even with some apparent variation in the data.

Some possible sources of error include the lack of tight control on the heaters used. Higher purity SCN would also improve the measurements. The purity of the SCN was not known exactly. It was most likely no better than 99.9% pure at the time of purchase and may have been even less pure after introduction to the sample container. Impurities have a strong effect on the surface tension and can also interfere with the laser beam corrupting the measurement.

5. CONCLUSIONS

Surface light scattering successfully determined non-invasively the surface tension of succinonitrile in the temperature range from 60 to 110°C. A temperature dependency was shown statistically. There was some variation in the test data, but much of this variation can be attributed to the control parameters of the experiment. Comparisons to the limited literature database showed that the regression fit of the experimental data was in between the two data sets found in the literature. Work is in progress for making these measurements with a sample

container temperature controller of better than 0.1° Kelvin with higher SCN purity and with SCN-acetone alloys.

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Table 1. Surface Tension (mN/m) of SCN measured with Surface Light Scattering Spectrometer as a function of temperature compared to values from the literature

Temperature °C	Data from SLS (Equation 6)	Lange Prediction	Walden Data
60	38.51	46.79	
65	38.19	46.25	
70	37.88	45.71	
75	37.56	45.17	
80	37.25	44.63	34.3
85	36.93	44.09	
90	36.62	43.55	
95	36.30	43.01	
100	35.99	42.47	32.7
110	35.36	41.39	
118	34.86	40.53	31.1

FIGURE CAPTIONS

Figure 1. Surface Light Scattering Spectrometer (Transmission Type)

Figure 2. Surface Light Scattering Spectrometer (Reflection Type)

Figure 3. Typical Time Correlation Function $R(\tau)$ and Residual to Nonlinear Least Squares Fit for SCN Liquid/Vapor Interface Using SLS Spectrometer

Figure 4. Typical Power Spectrum with Residual Fit for SCN Liquid/Vapor Interface Using SLS Spectrometer

Figure 5. Surface Tension of SCN as a Function of Temperature

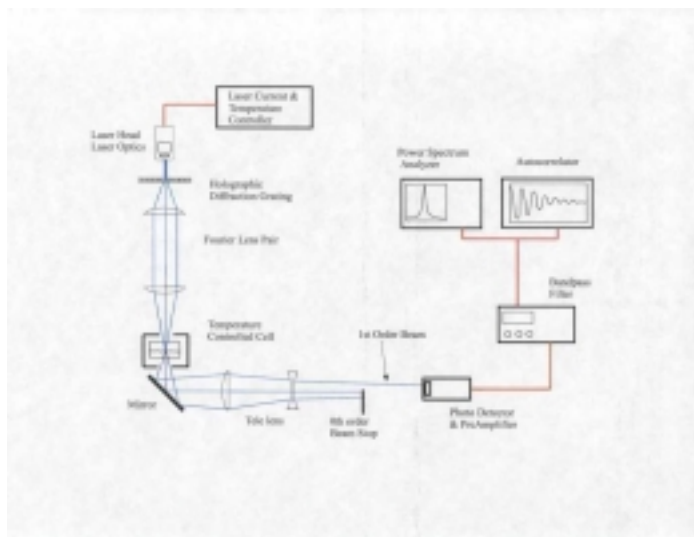


Figure (1) Surface Light Scattering Spectrometer
(Transmission Type)

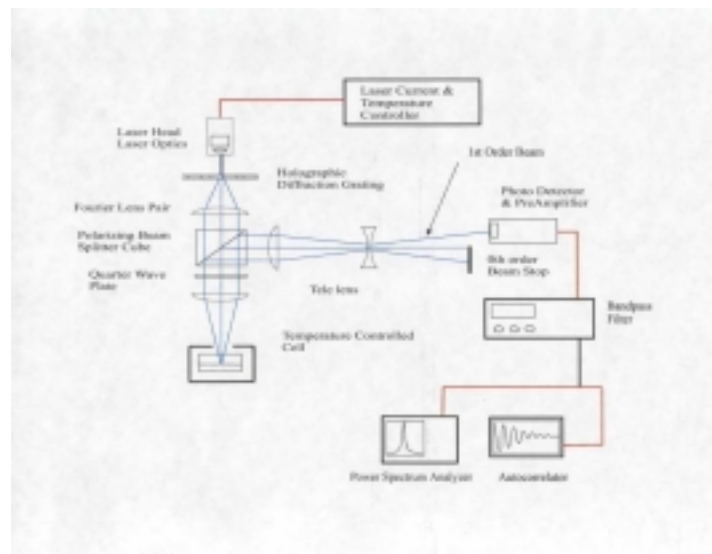


Figure (2) Surface Light Scattering Spectrometer
(Reflection Type)

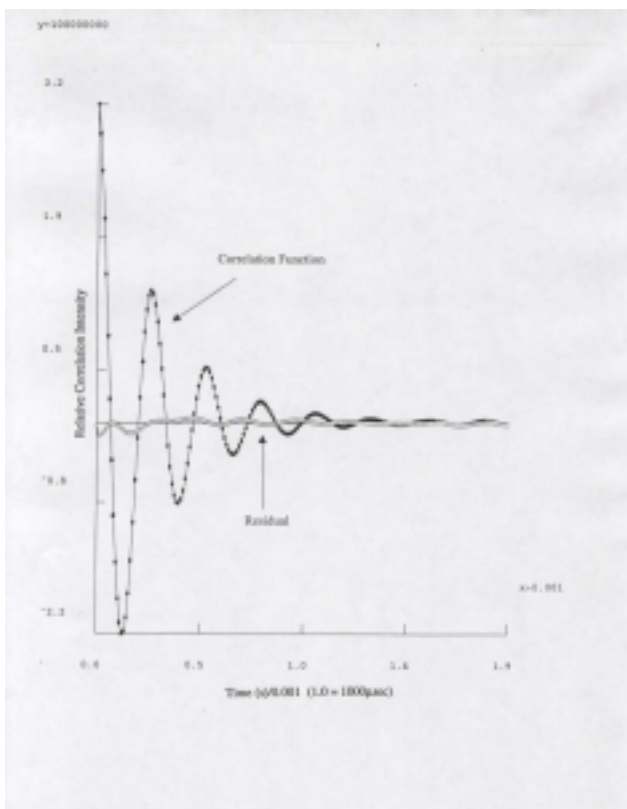


Figure 3. Typical Time Correlation Function $R(\tau)$ and Residual
to Nonlinear Least Squares Fit for SCN Liquid/Vapor
Interface Using SLS Spectrometer

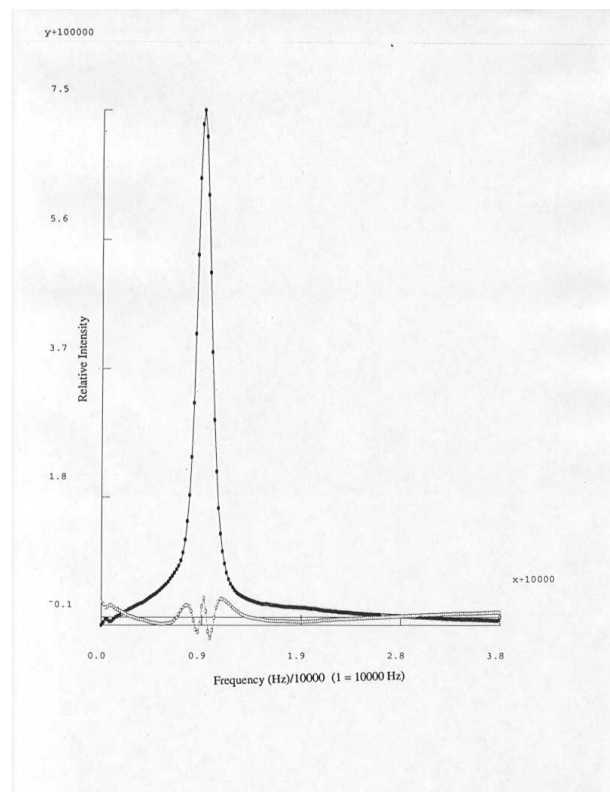


Figure 4. Typical Power Spectrum with Residual
Fit for SCN Liquid/Vapor Interface Using
SLS Spectrometer

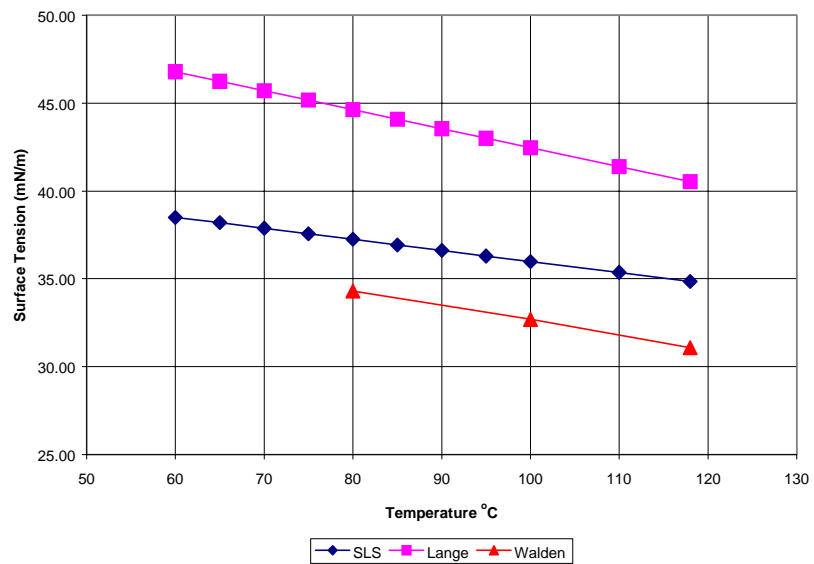


Figure (5) Surface tension of SCN as a Function of Temperature